

Supporting Information for
Experimental and Theoretical Investigation of the Antiferromagnetic
Coupling of Cr^{III} Ions through Diamagnetic –O–Nb^V–O– Bridges

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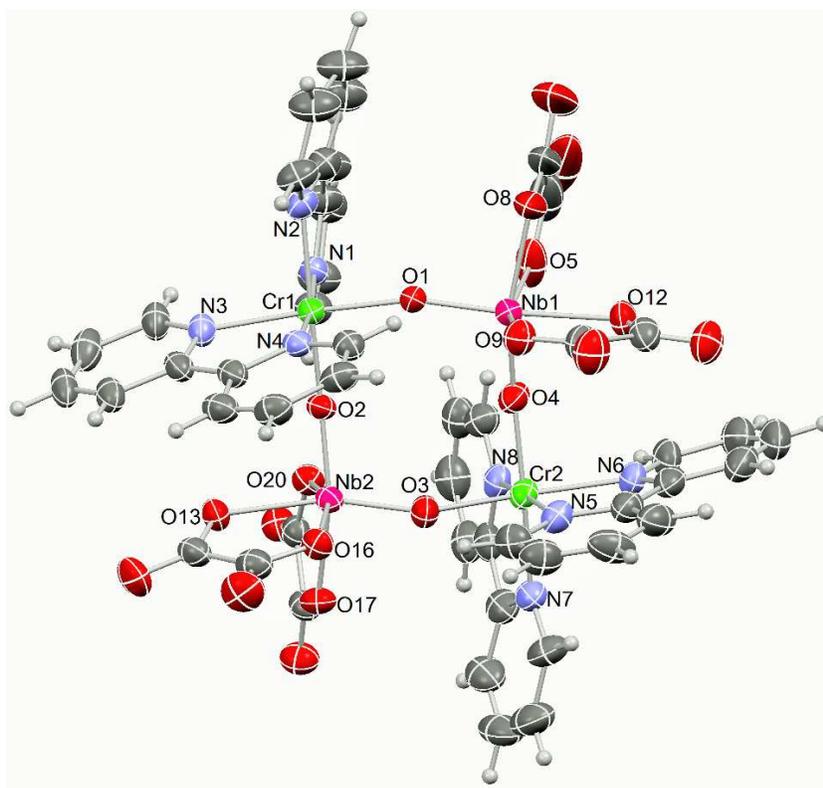


Figure S1. ORTEP-III³² drawing of molecule [Cr₂(bpy)₄(μ-O)₄Nb₂(C₂O₄)₄] in **1**, with the metal and coordinated O,N atom-numbering. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are depicted as spheres of arbitrary radii.

Table S1. Geometric Parameters (Å, deg) of the Cr1 Coordination Sphere at 293 K and 90 K, and after a DFT Geometric Optimization (Relaxing only the Atomic Positions of an Isolated Molecule Placed in a Cubic Box)

	293 K	90 K	DFT
Cr1–O2	1.909(2)	1.912(4)	1.907
Cr1–O1	1.921(2)	1.922(4)	1.911
Cr1–N4	2.053(3)	2.042(4)	2.094
Cr1–N1	2.057(3)	2.050(4)	2.103
Cr1–N2	2.069(3)	2.068(4)	2.141
Cr1–N3	2.082(3)	2.064(5)	2.139
O2–Cr1–O1	92.52(10)	92.01(17)	94.4
O2–Cr1–N4	89.82(11)	89.51(16)	88.0
O2–Cr1–N1	95.23(11)	95.17(16)	97.3
O2–Cr1–N2	173.90(12)	173.95(17)	174.5
O2–Cr1–N3	86.36(11)	86.37(17)	85.8
O1–Cr1–N4	94.56(11)	94.31(16)	95.9
O1–Cr1–N1	90.66(11)	90.42(16)	89.7
O1–Cr1–N2	86.90(11)	87.07(19)	84.7
O1–Cr1–N3	173.13(12)	173.05(17)	173.4
N4–Cr1–N1	172.57(12)	173.23(17)	172.0
N4–Cr1–N2	96.28(12)	96.52(17)	97.5
N4–Cr1–N3	78.67(12)	78.93(17)	77.5
N1–Cr1–N3	96.19(12)	96.46(17)	96.9
N1–Cr1–N2	78.71(12)	78.86(17)	77.2
N2–Cr1–N3	94.95(12)	95.2(2)	95.7

Table S2. Geometric Parameters (Å, deg) of the Cr₂ Coordination Sphere at 293 K and 90 K, and after a DFT Geometric Optimization (Relaxing only the Atomic Positions of an Isolated Molecule Placed in a Cubic Box)

	293 K	90 K	DFT
Cr2–O4	1.900(3)	1.897(4)	1.908
Cr2–O3	1.905(3)	1.907(4)	1.909
Cr2–N5	2.039(3)	2.041(6)	2.091
Cr2–N7	2.057(3)	2.050(6)	2.140
Cr2–N6	2.059(3)	2.051(5)	2.131
Cr2–N8	2.059(3)	2.059(4)	2.097
O4–Cr2–O3	92.05(11)	91.87(18)	94.1
O4–Cr2–N5	91.43(12)	91.2(2)	91.0
O4–Cr2–N7	173.63(12)	174.2(2)	173.1
O4–Cr2–N6	88.88(12)	88.7(2)	86.6
O4–Cr2–N8	95.06(12)	95.17(18)	95.8
O3–Cr2–N5	94.55(12)	94.6(2)	95.2
O3–Cr2–N7	88.18(12)	87.6(2)	86.1
O3–Cr2–N6	173.33(13)	173.7(2)	173.0
O3–Cr2–N8	88.55(12)	88.09(17)	89.9
N5–Cr2–N7	94.90(13)	94.7(2)	95.9
N5–Cr2–N6	78.82(13)	79.0(2)	77.8
N5–Cr2–N8	172.71(12)	173.0(2)	171.3
N7–Cr2–N6	91.63(12)	92.4(2)	94.0
N7–Cr2–N8	78.58(13)	79.0(2)	77.4
N6–Cr2–N8	97.96(13)	98.2(2)	97.0

Table S3. Geometric Parameters (Å, deg) of the Nb1 Coordination Sphere at 293 K and 90 K, and after a DFT Geometric Optimization (Relaxing only the Atomic Positions of an Isolated Molecule Placed in a Cubic Box)

	293 K	90 K	DFT
Nb1–O4	1.798(3)	1.800(4)	1.872
Nb1–O1	1.800(2)	1.801(4)	1.870
Nb1–O5	2.029(4)	2.031(5)	2.081
Nb1–O9	2.058(3)	2.053(4)	2.093
Nb1–O8	2.160(4)	2.154(4)	2.132
Nb1–O12	2.181(3)	2.176(4)	2.154
O4–Nb1–O1	102.24(11)	102.44(18)	100.2
O4–Nb1–O5	92.66(13)	92.1(2)	89.2
O4–Nb1–O9	101.95(12)	101.77(17)	103.4
O4–Nb1–O8	162.86(14)	162.1(2)	161.4
O4–Nb1–O12	88.46(11)	88.32(17)	88.0
O1–Nb1–O5	102.44(11)	102.4(2)	100.7
O1–Nb1–O9	92.23(11)	92.70(17)	87.7
O1–Nb1–O8	92.14(14)	92.09(19)	91.8
O1–Nb1–O12	164.01(11)	164.34(16)	161.1
O5–Nb1–O9	156.67(13)	156.9(2)	163.4
O5–Nb1–O8	74.97(15)	74.4(2)	74.5
O5–Nb1–O12	88.72(12)	88.42(19)	96.4
O9–Nb1–O8	86.57(13)	87.75(19)	91.2
O9–Nb1–O12	73.76(11)	73.78(16)	73.8
O8–Nb1–O12	79.60(14)	79.75(18)	85.0

Table S4. Geometric Parameters (Å, deg) of the Nb₂ Coordination Sphere at 293 K and 90 K, and after a DFT Geometric Optimization (Relaxing only the Atomic Positions of an Isolated Molecule Placed in a Cubic Box)

	293 K	90 K	DFT
Nb2–O3	1.797(3)	1.794(4)	1.872
Nb2–O2	1.799(2)	1.797(4)	1.865
Nb2–O16	2.052(3)	2.053(4)	2.070
Nb2–O20	2.069(2)	2.067(4)	2.099
Nb2–O17	2.152(3)	2.147(4)	2.135
Nb2–O13	2.159(3)	2.149(4)	2.151
O3–Nb2–O2	102.34(11)	102.00(18)	99.8
O3–Nb2–O16	92.14(11)	91.88(18)	91.0
O3–Nb2–O20	103.40(11)	103.18(17)	102.9
O3–Nb2–O17	88.90(11)	89.16(17)	89.3
O3–Nb2–O13	162.42(11)	162.93(17)	163.6
O2–Nb2–O16	102.24(10)	102.92(15)	102.3
O2–Nb2–O20	90.00(10)	89.78(15)	87.0
O2–Nb2–O17	162.21(10)	162.39(16)	160.6
O2–Nb2–O13	91.92(10)	91.77(17)	90.9
O16–Nb2–O20	157.79(10)	157.85(15)	161.8
O16–Nb2–O17	90.93(10)	90.11(15)	94.6
O16–Nb2–O13	74.61(10)	74.96(15)	74.5
O20–Nb2–O17	73.85(10)	74.29(15)	74.1
O20–Nb2–O13	86.65(10)	86.73(15)	89.9
O17–Nb2–O13	79.98(10)	80.08(15)	84.4

Table S5. Geometric Parameters (Å, deg) Describing {Cr₂(μ-O)₄Nb₂} Core in 1 at 293 K and 90 K, and after a DFT Geometric Optimization (Relaxing only the Atomic Positions of an Isolated Molecule Placed in a Cubic Box)

	293 K	90 K	DFT
Cr1–O1–Nb1	162.75(15)	162.4(2)	165.3
Cr2–O4–Nb1	166.43(16)	167.7(2)	168.2
Cr1–O2–Nb2	174.33(14)	174.5(2)	177.4
Cr2–O3–Nb2	158.53(16)	158.6(3)	161.9
Cr1···Cr2	5.406(2)	5.412(2)	5.434
Cr1···Nb1	3.6790(14)	3.6789(16)	3.749
Cr1···Nb2	3.7033(14)	3.7049(16)	3.772
Cr2···Nb1	3.6722(14)	3.6762(16)	3.760
Cr2···Nb2	3.6378(14)	3.6370(17)	3.734
Nb1···Nb2	4.9622(8)	4.9577(19)	5.170

Table S6. Hydrogen–Bonding Geometry (Å and deg) in Compound 1 at 293 K and 90 K

Comp., <i>T</i>	<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>	Symm. op. on <i>A</i>
1, 293 K	O21–H21A···O8	0.85(11)	2.54(1)	2.971(9)	113(10)	$x, -1/2 + y, 1/2 - z$
	O21–H21B···O11	0.87(8)	2.11(1)	2.841(11)	141(10)	$-1/2 + x, -y, 1/2 - z$
	O22–H22A···O19	0.86(5)	1.99(5)	2.840(6)	170(12)	$1/2 + x, -1/2 - y, z$
	O22–H22B···O7	0.86(8)	2.03(8)	2.868(9)	168(7)	$1/2 + x, -y, 1/2 - z$
	O23–H23A···O14	0.85(9)	2.19(8)	3.003(7)	160(9)	$2 - x, -y, -z$
	O23–H23B···O10	0.88(9)	1.97(9)	2.828(7)	164(8)	$1/2 + x, 1/2 - y, z$
1, 90 K	O21–H21A···O8	0.90(2)	2.4(2)	2.944(12)	126(14)	
	O21–H21B···O11	0.87(12)	2.00(13)	2.835(13)	159(15)	$-1/2 + x, -1/2 - y, z$
	O22–H22A···O19	0.85(5)	1.99(5)	2.810(7)	160(8)	$x, -1/2 + y, -1/2 - z$
	O22–H22B···O7	0.86(6)	1.98(6)	2.848(10)	180(11)	$1/2 + x, -y, 1/2 - z$
	O23–H23A···O14	0.856(11)	2.13(11)	2.962(8)	161(10)	
	O23–H23B···O10	0.86(8)	1.94(8)	2.794(8)	174(11)	$-1/2 + x, -1/2 - y, z$

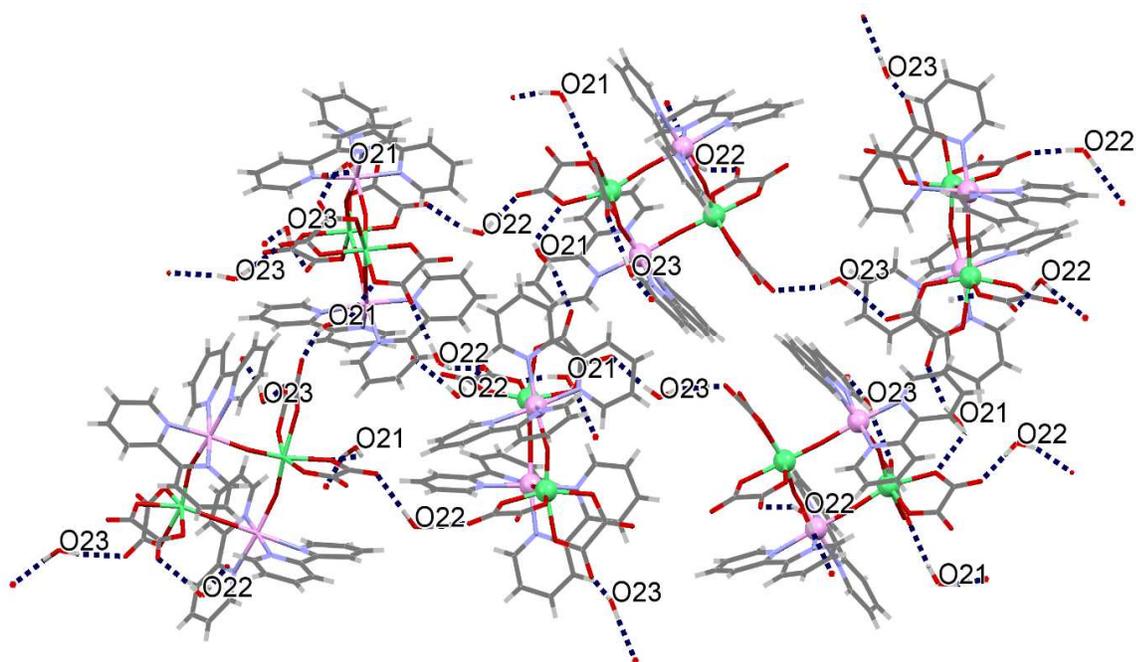


Figure S2. Hydrogen-bonding pattern in compound **1**: every water molecule connects two tetranuclear $[\text{Cr}_2(\text{bpy})_4(\mu\text{-O})_4\text{Nb}_2(\text{C}_2\text{O}_4)_4]$ units; the overall hydrogen bonding is three dimensional.

Table S7. Geometric Parameters of the Aromatic Stacking Interactions (\AA and deg) for **1 at 293 K and 90 K**

Compound, T	$\text{Cg}(i)^a \cdots \text{Cg}(j)$	$\text{Cg}(i) \cdots \text{Cg}(j)$	α^b	β^c	$\text{Cg}(i) \cdots \text{plane}[\text{Cg}(j)]$	Symm. op. on
1 , 293 K	(N3 \rightarrow C15) \cdots (N6 \rightarrow C30)	3.843(3)	13.8(2)	24.24	3.4291(19)	$-1 + x, y, z$
1 , 90 K	(N3 \rightarrow C15) \cdots (N6 \rightarrow C30)	3.732(4)	13.7(3)	23.90	3.372(3)	$-1 + x, y, z$

^a Cg = centre of gravity of the aromatic ring. ^b α = angle between the planes of two aromatic rings.

^c β = angle between the $\text{Cg} \cdots \text{Cg}$ line and the normal to the plane of the first aromatic ring

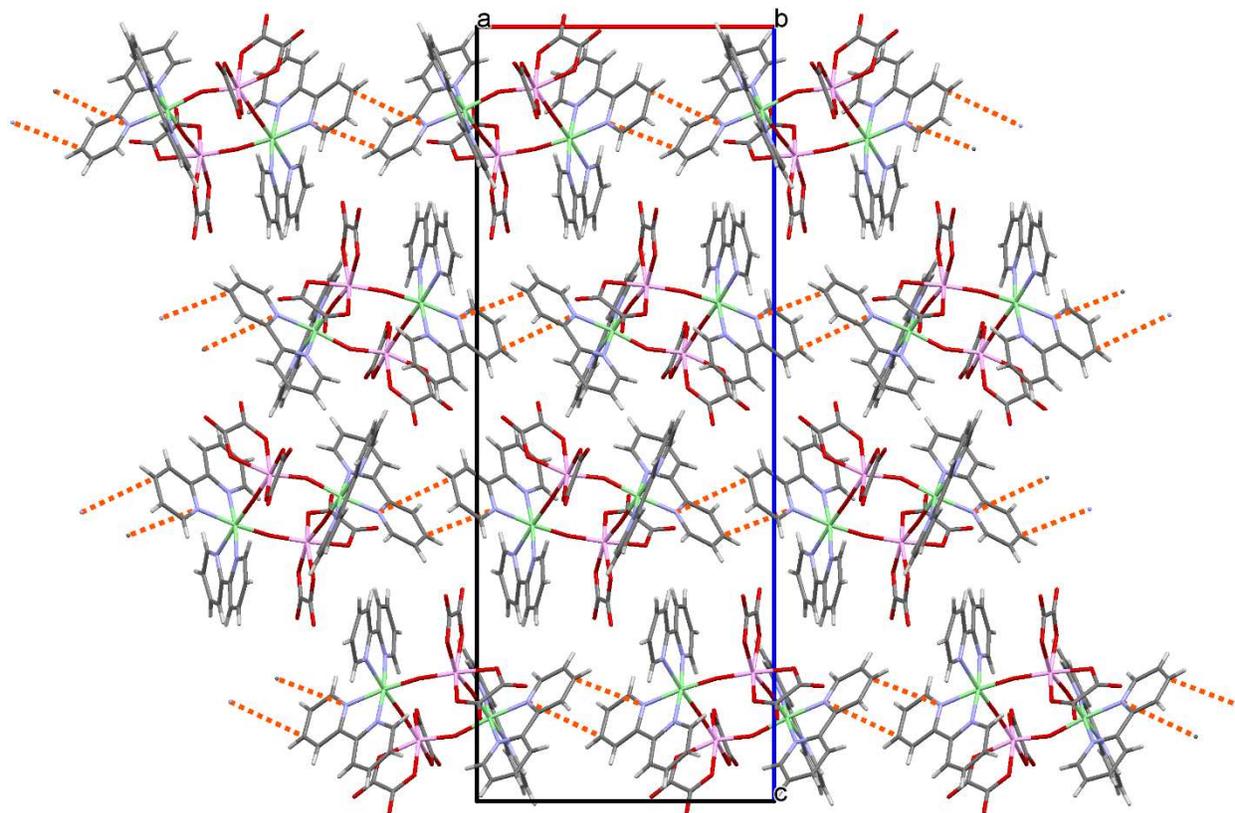


Figure S3. Aromatic stacking interactions between tetranuclear $[\text{Cr}_2(\text{bpy})_4(\mu\text{-O})_4\text{Nb}_2(\text{C}_2\text{O}_4)_4]$ units in **1**.

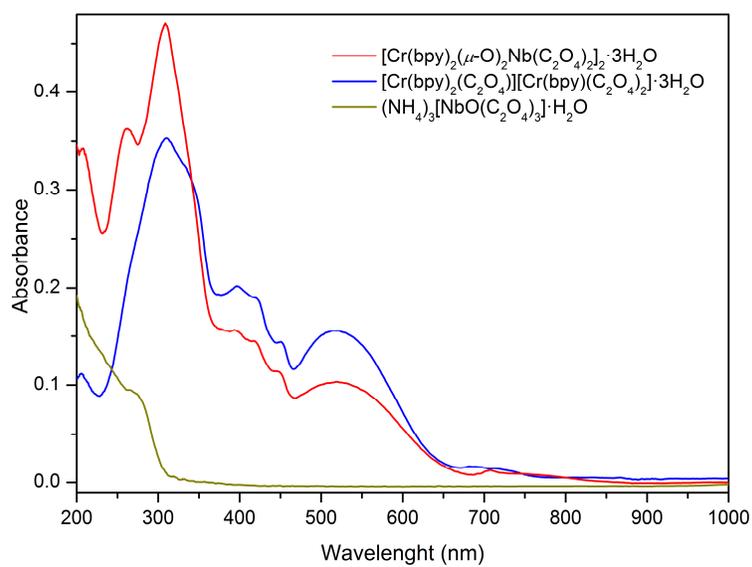


Figure S4. Solid state UV/Vis spectrum of compounds $[\text{Cr}_2(\text{bpy})_4(\mu\text{-O})_4\text{Nb}_2(\text{C}_2\text{O}_4)_4] \cdot 3\text{H}_2\text{O}$ (**1**), $[\text{Cr}(\text{bpy})_2(\text{C}_2\text{O}_4)][\text{Cr}(\text{bpy})(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ and $(\text{NH}_4)_3[\text{NbO}(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$.